United States Patent

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Rochester, N.Y.

[54] PHOTOGRAPHIC PROCESS AND ELEMENT FOR THE PRODUCTION OF ADD-ON IMAGES

19 Claims, No Drawings

[52] U.S. Cl. 96/49, 96/27, 96/13
[51] Int. Cl. G03c 5/18, G03c 7/34
[50] Field of Search ..... 96/13, 35, 33, 38.2, 38.5, 49, 89, 91 D, 27, 91 R

[56] References Cited

UNITED STATES PATENTS

2,993,788	7/1961	Straw et al.	96/13

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ABSTRACT: Photographic add-on images are prepared by overcoating a hydrophilic colloid layer having an image therein with a hydrophobic light-sensitive layer to prepare a photographic element, imagewise exposing the light-sensitive layer and developing an image therein without impairing the underlying hydrophilic image-containing layer. The add-on images so produced are susceptible of convenient removal by treatment of the hydrophobic layer with a solvent which is not a solvent for the hydrophilic colloid layer. Alternatively, when a hydrophobic strippable layer is interposed between the hydrophobic layer and light-sensitive hydrophobic layer, the hydrophobic layers including the add-on photographic image can be removed by physically stripping them from the hydrophilic layer. Image removal is accomplished without substantially impairing the image in the hydrophilic colloid layer.

PHOTOGRAPHIC PROCESS AND ELEMENT FOR THE PRODUCTION OF ADD-ON IMAGES

This invention relates to photography and more particularly to the production of add-on photographic images and to a process for the production of such add-on photographic images.

The image-forming arts, including purely mechanical means like drawing and printing such as offset printing including lithographic printing and the like, as well as photomechanical printing such as photolithography, are well known. Additionally, the photographic image-forming arts are likewise well known, and by utilizing one or more of these techniques, one is able to prepare visible images which are typically carried on a support material. It is also known to form subsequent, add-on printed or otherwise stamped images over an existing image produced, for example, by one of the image-forming techniques noted hereinabove. Add-on images formed by a means such as printing can involve intricate apparatus and consume considerable time, and the images so produced are generally permanent once applied. The present invention relates to the convenient, photographic formation of add-on images, which images can be subsequently substituted or deleted if desired.

Accordingly, it is an object of this invention to provide novel photographic processes for the preparation of add-on images.

Another object of the present invention is to provide new photographic processes for the preparation and removal of add-on images.

Still another object of this invention is to provide a novel photographic process for the preparation and removal of add-on images without the impairment of an underlying image.

Yet an additional object of the instant invention is to provide a new photographic element adapted to the preparation of add-on photographic images.

Still additional objects of this invention will become apparent from a reading of the following specification and appended claims.

The objects of the present invention are accomplished with a process for preparing an add-on photographic image on a support material having thereon an image in a hydrophilic colloid layer, the process comprising the steps of coating a hydrophobic, radiation-sensitive composition over a portion of the hydrophilic colloid layer, imagewise exposing the hydrophobic light-sensitive composition, and thereafter developing a visible photographic image in the hydrophobic composition without substantially impairing the image in the hydrophilic colloid layer.

The photographic processes and elements of this invention are susceptible of a wide variety of advantageous uses such as, for example, the updating of data files like those for social security numbers, various license numbers, addresses and other information which is often changed. A special type of updating for which the processes and elements of this invention are adapted is the correction, editing or other updating of aerial reconnaissance photographs. While utilizing one master photograph or other original image material, variable features such as weather information, military installations, etc., can be continually and conveniently revised. By means of the instant invention, the usefulness of an original is extended many times.

Supports useful in this invention include such materials as conventional photographic film base materials like cellulose esters such as cellulose acetate, cellulose triacetate, cellulose acetate butyrate, etc., poly-α-olefins like polyethylene and polypropylene, polycarbonates, polyesters such as poly(ethylene terephthalate) as well as metals such as zinc and aluminum and paper including polyethylene and polypropylene-coated papers. Other support materials that are suitably used herein are known in the art.

In the present invention, a support material such as those described hereinabove has thereon an image carried in a hydrophilic colloid layer. The images are advantageously visible images, such as those of photographic silver or a photographically produced colored dye. Additional visible images include for example those of an ink or other suitable contrasting image defining material. Such images likewise include latent photographic images like those which are susceptible of convenient intensification to a visible image by, for example, treatment with a suitable development environment such as heat or a chemical developer composition. Latent images are particularly advantageous where it is desirable to transmit data in a confidential fashion, since the image would be substantially invisible prior to intensification.

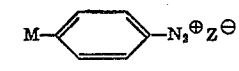
The images described immediately hereinabove are advantageously carried in a hydrophilic colloid layer which serves as a binder and carrier vehicle. Desirable hydrophilic colloids include any of the water-permeable binding materials suitable for this purpose, such as gelatin, colloidal albumen, polyvinyl compounds, cellulose derivatives, acrylamide polymers and the like, either alone or in combination and mixture.

According to the processes of this invention, a support material having thereon an image in a hydrophilic colloid layer, including such support images and colloids as are described elsewhere herein, is coated with a hydrophobic, radiation-sensitive composition over a portion of the hydrophilic colloid layer.

Coating is advantageously accomplished by a wide variety of techniques including such means as brushing, flow coating, swabbing, hopper coating, doctor blade coating and the like, with the choice of one particular coating method being governed largely by the requirements of any given coating situation. Where desirable coating techniques other than those specifically noted, such as whirler coating and the like, can be utilized. The coated hydrophobic, radiation-sensitive composition includes a hydrophobic, radiation-sensitive composition alone or a radiation-sensitive composition dispersed in a hydrophobic film-forming binder material such as those described hereinbelow. The term radiation-sensitive refers to a responsiveness to activating electromagnetic radiation including, but not limited to, visible light rays. Other activating radiation includes such means as gamma rays, X-rays, ultraviolet rays, infrared radiation and the like.

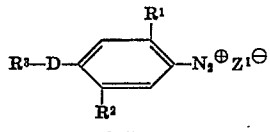
Advantageous hydrophobic, radiation-sensitive photographic compositions typically include those compositions which are conveniently coated, stable upon storage, and easily developed to yield a resultant photographic image. Particularly advantageous photographic image-forming compositions include diazo-type compositions, furfurylidene compositions, compositions containing a protected aldehyde and compositions containing a leuco dye base.

Advantageously employed diazo-type compositions typically include a diazonium salt and a coupler compound which can react with the diazonium salt to form an azo dye. Typical diazonium salts include benzene diazonium salts such as those having the formula:



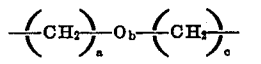
wherein M is either a hydrogen atom, a halogen atom, an aryl radical, an amino radical (including substituted amino radicals) or a thioether radical and Z is an anion. These compounds can also be substituted on one or more of the nuclear carbons with at least one of either a halogen atom, an alkyl radical, an alkoxy radical, an acyl radical, a carbamyl radical, a carboxyl radical or a nitro radical.

Particularly useful diazonium salts include benzene diazonium salts having the formula as described above wherein M is either an amino radical including substituted amino radicals or a thioether radical, and wherein the benzene nucleus is unsubstituted or substituted in at least one of the 2-position and the 5-position with either an alkyl radical or an alkoxy radical. This class of useful diazonium salts can be represented by the formula:



wherein:

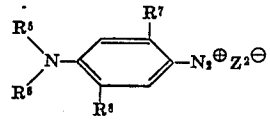
1. D is either a sulfur atom or a radical having the formula NR^4,
2. R^3, when taken alone, is either a hydrogen atom when D is NR^4, or a lower alkyl radical, a lower alkoxy radical, a lower acyl radical, an aryl radical having a nucleus of 6 carbon atoms, or an aralkyl radical when D is either a sulfur atom or NR^4,
3. R^4, when taken alone, is either a hydrogen atom, a lower alkyl radical or a lower alkoxy radical,
4. R^3 and R^4, when taken together, complete a divalent radical having the formula:



wherein *b* is an integer having a value of 0 or 1, each of *a* and *c* is a positive integer, and the sum of *a*, *b* and *c* has a value of 5,

5. R^1 and R^2 are each either a hydrogen atom, a lower alkyl radical (preferably methyl or ethyl) or a lower alkoxy radical (preferably methoxy or ethoxy), and
6. $Z^{1\ominus}$ is an anion.

Preferred benzene diazonium salts include the substituted aminobenzene diazonium salts having the formula:



wherein:

1. each of R^5 and R^6, when taken alone, is a lower alkyl radical,
2. R^5 and R^6, when taken together, are the number of carbon and hetero oxygen atoms necessary to complete a morpholino radical,
3. each of R^7 and R^8 is either a hydrogen atom, a lower alkyl radical or a lower alkoxy radical, and
4. Z^2 is either a chlorozincate anion, a fluoroborate anion or a chlorostannate anion.

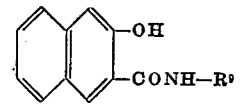
The most preferred benzene diazonium salts are the fluoroborate salts wherein:

1. R^7 and R^8 are alkoxy radicals when R^5 and R^6 complete a morpholino radical, and
2. R^7 and R^8 are each a hydrogen atom when R^5 and R^6 are each a lower alkyl radical.

Illustrative of the subject diazonium salts are such compounds as the salts of 1-diazo-2,5-dimethoxybenzene; 1-diazo-2,5-diethoxybenzene; 1-diazo-4-chloro-2,5-diethoxybenzene; 4-diazo-2,5-dimethoxybiphenyl; 4-diazo-2,5,4'-triethoxybiphenyl; 1-diazo-4-dimethylaminobenzene; 1-diazo-4-(diethoxyamino)benzene; 1-diazo-4-[bis(hydroxypropyl)amino]benzene; 1-diazo-4-N-methyl-N-allylamino)benzene; 1-diazo-4-(diamylamino)benzene; 1-diazo-4-(oxazolidino)benzene; 1-diazo-4-(cyclohexylamino)benzene; 1-diazo-4-(9-carbazolyl)benzene; 1-diazo-4-(dihydroxyethylamino)-3-methylbenzene; 1-diazo-4-dimethylamino-3-methylbenzene; 1-diazo-2-methyl-4-(N-methyl-N-hydroxypropylamino)benzene; 1-diazo-4-dimethylamino-3-ethoxybenzene; 1-diazo-4-diethylamino-3-chlorobenzene; 1-diazo-2-carboxy-4-dimethylaminobenzene; 1-diazo-3-(2-hydroxyethoxy)-4-pyrrolidinobenzene; 1-diazo-2,5-diethoxy-4-acetoxyaminobenzene; 1-diazo-4-methylamino-3-ethoxy-6-chlorobenzene; 1-diazo-2,5-dichloro-4-benzylaminobenzene; 1-diazo-4-phenylaminobenzene; 1-diazo-4-morpholinobenzene; 1-diazo-4-morpholino-3-methoxybenzene; 1-diazo-4-morpholino-2,5-dimethoxybenzene; 1-diazo-4 -morpholino-2-ethoxy-5-methoxybenzene; 1-diazo-4-morpholino-2,5-dibutoxybenzene; 1-diazo-2,5-diethoxy-4-benzoylaminobenzene; 1-diazo-2,5-dibutoxy-4-benzoylaminobenzene; 1-diazo-4-ethylmercapto-2,5-diethxoybenzene; 1-diazo-4-tolylmercapto-2,5-diethoxybenzene and the like.

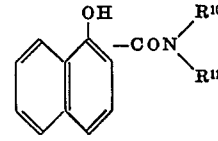
Azo dye couplers which can be reacted with the benzene diazonium salt to form an azo dye include those disclosed by Kosar, "Light-Sensitive Systems," John Wiley & Sons, Inc., New York (1965), pp. 220–240. Phenolic couplers are preferred, however, with particularly preferred classes including:

1. as blue couplers, 2-hydroxy-3-naphthanilides having the formula:



wherein R^9 is a phenyl radical, and preferably a phenyl radical substituted with at least one of either a lower alkyl radical or a lower alkoxy radical or a halogen atom;

2. as yellow couplers, 1-hydroxy-2-naphthamides having the formula:

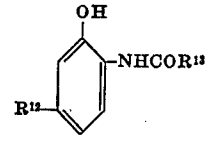


wherein:

a. each of R^{10} and R^{11} when taken alone, is either a hydrogen atom or an alkyl radical, a cycloalkyl radical, an aryl radical, an aralkyl radical and the like hydrocarbon or substituted hydrocarbon radicals,

b. R^{10} and R^{11} when taken together represent the carbon and oxygen atoms necessary to complete a six-membered hetero piperidino or morpholino radical, and

3. as yellow couplers, 2-acylamido-5-substituted phenols having the formula:



wherein R^{12} is either an alkyl radical or an alkoxy radical and R^{13} is either an alkyl radical, an aryl radical, an aralkyl radical or an aralkoxy radical.

Illustrative of the subject couplers are such compounds as for example, 2-hydroxy-3-naphthanilide; 2-hydroxy-2'-methyl-3-naphthanilide; 2-hydroxy-2',2'-dimethoxy-5'-chloro-3-naphthanilide; 2-hydroxy-2'-dimethoxy-3-naphthanilide; 2-hydroxy-2',5'-dimethoxy-4'-chloro-3-naphthanilide; 2-hydroxy-1'-naphthyl-3-naphthanilide; 2-hydroxy-2'-naphthyl-3-naphthanilide; 2-hydroxy-4'-chloro-3-naphthanilide; 2-hydroxy-3-naphthanilide; 2-hydroxy-2',5'-dimethoxy-3-naphthanilide; 2-hydroxy-2',4'-dimethyl-3-naphthanilide; 1-hydroxy-2-naphthamide; N-methyl-1-hydroxy-2-naphthamide; N-butyl-1-hydroxy-2-naphthamide; N-octadecyl-1-hydroxy-2-naphthamide; N-phenyl-1-hydroxy-2-naphthamide; N-methyl-N-phenyl-1-hydroxy-2-naphthamide; N-(2-tetradecyloxyphenyl)-1-hydroxy-2-naphthamide; N-[4-(2,4di-tert-amylphenoxy)butyl]-1-hydroxy-2-naphthamide; 1-hydroxy-2-naphthopiperidide; N-(3,5-dicarboxyphenyl)-N-ethyl-1-hydroxy-2-naphthamide; N,N-dibenzyl-1-hydroxy-2-naphthamide; N-(2-chlorophenyl)-1-hydroxy-2-

naphthamide; N-(4-methoxyphenyl)-1-hydroxy- 2-naphthamide; 1-hydroxy-2-naphthopiperazide; 1,3-bis(1-hydroxy-2-naphthamido-benzene); 2-acetamido-5-methylphenol; 2-acetamido-5-pentadecylphenyl; 2-butyramido-5-methylphenol; 2-(2,4di-tert-amylphenoxy-acetamido)-5-methylphenol; 2-benzamido-5-methylphenol and the like.

For ease of coating and stability of the coated layer, the diazo-type composition is generally dispersed in a polymeric matrix such as those described hereinbelow, conventionally in an amount of from about 20 to about 40 parts by weight per 100 parts of matrix polymer.

In addition to the dye-forming components, the diazo-type composition can contain and usually does contain other additives such as ultraviolet absorbers, poly (vinyl and the like to advantageously modify its photographic and chemical 4--hydroxy-3 A preferred class of additives includes the known acid stabilizers which operate to prevent premature coupling of the diazonium salt and coupler compound. These acid stabilizers include organic acids such as 5-sulfosalicyclic acid and the like. In general, an organic acid stabilizer is preferably present in all of the diazo-type reproduction media of this invention, with the amount normally varying from about 1 part to about 6, and preferably from about 2 to about 5 parts by weight per 100 parts of polymeric matrix. Additionally, metal salts like zinc chloride can also be present as a development accelerator or a dye brightener, generally in an amount of from about 0.5 to about 1.5 parts by weight per 100 parts of matrix polymer.

Another, and especially desirable, class of additives for diazo-type compositions are hindered phenols containing, in the 2-position, either an alkyl or a cycloalkyl radical and in the 4-position, either an alkyl radical, an alkoxy radical, a hydroxyl radical or a thioether radical which, with the hindered phenolic moiety completes a hindered bisthiophenol and more generally a symmetrical bisthiophenol. These hindered phenols operate to restrain fading of the image azo dye. Such advantageous hindered phenols are described in detail in copending U.S. Pat. application Ser. No. 663,470, filed July 31, 1967.

Furfurylidene compositions which are advantageous radiation-sensitive compositions in the hydrophobic compositions described herein include those photographic image-forming compositions having a haloalkane sensitizer which is preferably a lower haloalkane, a primary aromatic amine as an image enhancer or speed accelerator and a furfurylidene derivative as a color-forming ingredient, which furfurylidene compound preferably includes at least two furan rings and also is desirably an imine or a cyclic acetal.

In general, the haloalkane sensitizer used is a solid at room temperature having a purity of at least 98 percent with compounds containing 1 to 2 carbon atoms being preferred such as iodoform and pentabromoethane. Iodoform and iodoform complexes such as iodoform-diethylamine are preferred.

The primary aromatic amine enhancer is prepared by conventional organic synthesis such as by the reduction of nitro compounds. The enhancer is preferably a solid at room temperature and has a boiling point preferably in excess of 200° C. (atmospheric pressure). It is desirably soluble in chloroform at room temperature to the extent of at least 10 percent. Its purity exceeds 98 percent.

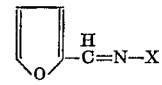
The aromatic amine enhancer, besides being a primary aromatic amine, preferably contains two primary amino groups each of which is in resonance with a benzene ring and more preferably, these amino groups are in the meta position on a single ring. The benzene ring may contain up to two other functional groups but preferably contains only one and it is further preferred that a functional group be adjacent to an amino group. The meta-phenylenediamines such as 1-chloro-2,4-phenylenediamine, and mono-substituted forms thereof with the substituent group being adjacent to an amino group are definitely preferred. 2,4-Toluenediamine and the 4,4'-dianilines also give exceptional performance as do the benzidines.

The furfurylidene color-former is conveniently prepared by reacting furfural with a suitable amine in the case of the furfurylidene imines and with a suitable glycol or higher polyol in the case of the cyclic acetals. Conventional, well understood organic synthesis techniques are used. The reaction is usually a condensation reaction carried out with an acidic catalyst in an organic solvent at temperatures in the range of 80° to 120° C. It is preferred to use furfurylidenes in the photographic medium that are crystalline solids at room temperature and have melting points in the range of 70° to 225° C., but liquid furfurylidenes which boil between 100° and 220° C. at 10 mm. Hg pressure can also be used. It is preferred that the furfurylidenes be soluble in $CHCl_3$ to the extent of at least 0.02 gms./gm. at 25° C.

It is important to thoroughly purify the furfurylidene after its preparation in order to rid it of dark color bodies and reaction tars that would unduly tone or destroy the clarity of the background areas of the photographic medium. Solvent extraction and crystallization techniques have proved to be adequate in most situations although chromatographic and other more advanced techniques can be used when necessary. Generally, speaking, if the purity of the furfurylidene color-former exceeds 98 weight percent, it is sufficiently pure for advantageous use in the processes described herein. The main criterion is that it be purified to the extent that it imparts no, or just a slight, tint of color when diluted and applied in the photographic medium. Some of the furfurylidene compounds are colored per se and may be used in situations where it is not necessary to have a white background. Where a white background or a substantially white background is desired, and the furfurylidene compound imparts a slight color or tint to the photographic medium, this may be masked by the addition of dyes to the medium or by slightly coloring the support for the photographic medium, as will be understood by those skilled in the art.

Additional detailed information pertaining to furfurylidene reproduction media and their preparation and chemical composition, including the recitation of preferred furfurylidene color formers such as:

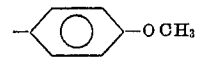
1. monofurfurylidenes having the formula:

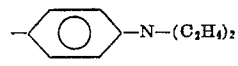


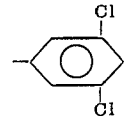
wherein X represents a radical selected from either:

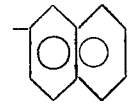
(a) —OH

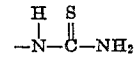
(b) 

(c) 

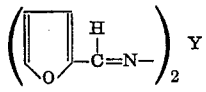
(d) 

(e) 

(f) 

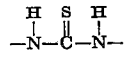
(g) 

2. difurfurylidenes having the formula:

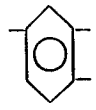


wherein Y represents:
(a) absent (azine structure)

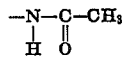
(b)



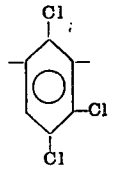
(c)



wherein Z^2 represents —H, —CH_3, or



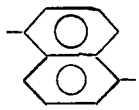
(d)



(e)



(f)

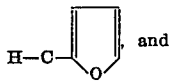


(g)

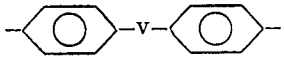


wherein each Z^3 is identical and reprenents either —H or CH_3

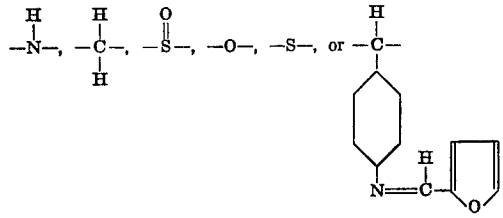
(h)



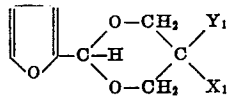
(i)



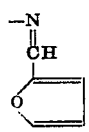
wherein V represents either



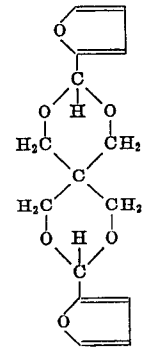
3. Cyclic acetal containing furfurylidenes including those having one furan ring such as those having the formula:



wherein X_1 is —CH_3 and Y_1 is —NO_2 or wherein X_1 is —CH_3 and Y_1 is

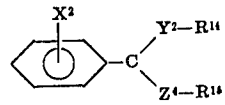


and those having two furan rings such as:

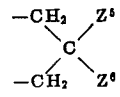


is included in U.S. Pats. 3,394,392; 3,394,393; and 3,394,395.

Radiation-sensitive compositions containing a protected aldehyde and useful in the process described herein typically include a haloalkane sensitizer which is preferably a lower haloalkane having 1 or 2 carbon atoms, a primary aromatic amine such as those described hereinabove as useful in furfurylidene compositions and a protected aldehyde type dye precursor such as those having the formula:



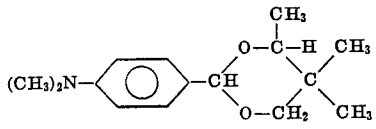
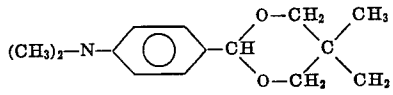
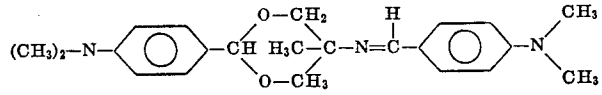
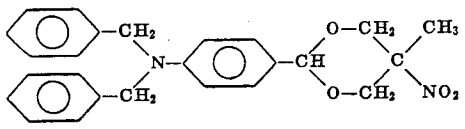
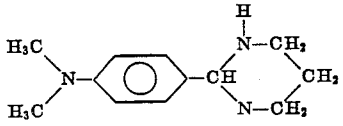
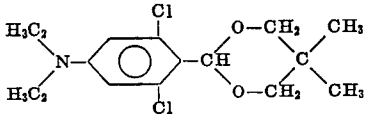
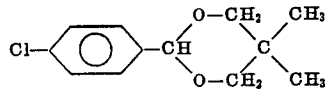
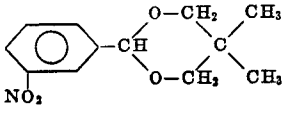
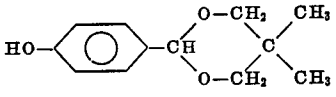
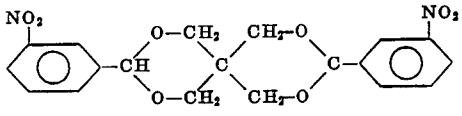
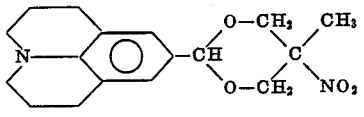
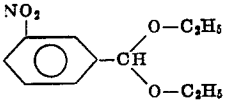
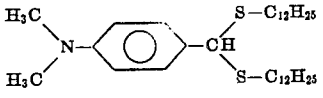
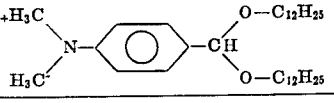
wherein X^2 represents at least one chromophoric or auxochromic group which is preferably in other than the ortho position. Y^2 and Z^4 represent either an oxygen atom, a sulfur atom or a nitrogen atom, with the proviso that only one is a nitrogen atom. R^{14} and R^{15} each represent an organic radical such as an aryl radical like phenyl or naphthyl, an alkyl radical typically having from 1 to 20 carbon atoms like methyl, ethyl, propyl, tertbutyl, amyl hexyl, octyl, dodecyl and the like. R^{14} and R^{15}, when considered together, preferably form a cyclic acetal structure such as one having the formula:



wherein Z^5 and Z^6 represent any suitable radical such as, for example, an alkyl radical.

The following table illustrates the chemical structures of advantageous protected aldehydes. Preferably, the protected aldehyde dye precursor is a crystalline solid at room temperature (about 20° C.) and has a melting point in the range of 40° to 225° C. It is desirably soluble in a suitable solvent system to permit convenient solvent coating onto a support material.

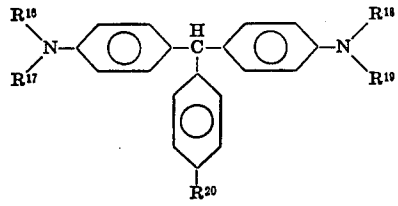
Especially preferred protected aldehydes include those of the chemical structures tabulated hereinbelow:

Compound No.	Chemical structure	Melting point, ° C.
1		76 to 77.5.
	2(4-dimethylaminophenyl)-4,5,5-trimethyl-1,1,3-dioxane.	
2		162 to 164.
3		200 to 203.
4		185.5 to 187.
5		76 to 78.
6		83 to 87.
7		55 to 56.
8		43 to 50.
9		White needles, 134 to 136.
10		130 to 135.
11		168 to 172.
12		170°/30 mm.
13		41 to 43.5.
14		White leaflets; melt near room temperature.

Additional detailed information pertinent to the chemical composition and preparation of reproduction media containing a protected aldehyde is contained in U.S. Pat. No. 3,410,687.

Advantageous radiation-sensitive compositions containing a leuco dye base typically include a leuco dye base and an activator compound or sensitizer. Leuco dye bases can be conveniently represented by DH_n wherein H represents a hydrogen atom, the removal of which forms a compound differently colored than DH_n, and n is an integer of from 1 to 2, with the proviso that when n is 1 and the resultant dye is cationic, the acid salt of the leuco form of the dye is used.

Especially useful leuco dye bases include those of triarylmethane dyes such as those leuco dye bases having the formula:



wherein R^{16}, R^{17}, R^{18} and R^{19} each represent either a hydrogen atom, an alkyl radical, an aryl radical or an aralkyl radical, and wherein R^{20} represents a member selected from a hydrogen atom and a radical having the formula:



wherein R^{21} and R^{22} are as described hereinabove.

In addition to the triphenylmethane dyes in the leuco form, other advantageous leuco compounds include the leuco form of such dyes as:

aminoxanthenes
aminothioxanthenes
amino-9,10-dihydroacridines
aminophenoxazines
aminophenothiazines
aminodihydrophenazines
aminodiphenylmethanes
leuco indamines
aminohydrocinnamic acids (cyanoethanes, leuco methines)
hydrazines
leuco indigoid dyes
amino-2,3-dihydroanthraquinones
tetrahalo-p,p'-bisphenols
2(p-hydroxyphenyl)-4,5-diphenylimidazoles
phenethylanilines

Exemplary leuco dyes of the above-noted types include those described in extensive detail in Canadian Pat. No. 785,714.

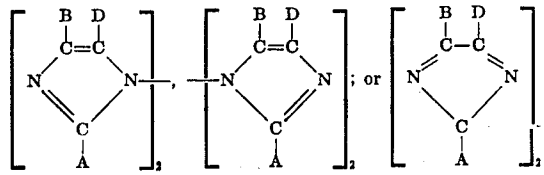
Activator compounds that are advantageously combined with the above-mentioned leuco compounds include, for example, compounds having a carbonyl moiety



such as alkyl ketones, aryl ketones, aldehydes and certain esters. Exemplary such activators include compounds like:

4'-ethylacetophenone
2', 6'-dimethoxyacetophenone
2',4'-dichloracetophenone
2',5'-dichloracetophenone
2',4'-dimethylacetophenone
3'-bromoacetophenone
2',5'-dimethylacetophenone
ethyl-o-benzoyl benzoate
phenyl-2-propanone
phenyl-2-pyridyl ketone
phenyl-2-thienyl ketone
β-naphthoylacetonitrile
2-pyridone
acetylacetone
α,α,α-tribromoacetophenone
α,α,α-tribromo-m-nitroacetophenone
benzaldehyde
phenylacetaldehyde
orthochlorobenzaldehyde
diethylphenylmalonate
ethylacetoacetate
ethylbenzoylacetate

Additional activators useful in combination with the leuco form of a dye are dimers of certain 2,4,5-triarylimidazolyl radicals. Included are 2,4,5-triarylimidazolyl dimers having a formula selected from:



wherein A, B and D are aryl radicals of homo and heterocyclic aromatic systems which can be alike or different and which can be substituted or unsubstituted. Representative aryl radicals are, for example, phenyl, tolyl, xylyl, naphthyl, thienyl and the like. Preferred 2,4,5-triarylimidazolyl radicals include such radicals as those set out on pages 12 to 18 of Canadian Pat. No. 785,714.

The above-identified radiation-sensitive compositions including the previously mentioned preferred light-sensitive diazo-type compositions, as well as the furfurylidene compositions, compositions containing a protected aldehyde and compositions containing the leuco form of a dye, are usually dispersed in a hydrophobic film-forming polymer matrix to prepare a composite hydrophobic, radiation-sensitive composition including light-sensitive compositions. The use of a polymer carrier vehicle operates to promote ease of coating and stability of the resultant sensitive layer. Additionally, the use of a hydrophobic vehicle promotes convenient removal of the hydrophobic layer without substantially impairing the underlying image in the hydrophilic layer.

Advantageous matrix polymers include a wide variety of polymeric substances such as, for example, cellulosic compounds like ethylcellulose, butylcellulose as well as cellulose esters like cellulose acetate, cellulose triacetate, cellulose butyrate and cellulose acetate butyrate; vinyl polymers such as

poly(vinyl acetate), poly(vinylidene chloride), poly(vinyl butyral), copolymers of vinyl chloride and vinyl acetate, polystyrenes, poly(methyl methacrylate), copolymers of alkylacrylates and acrylic acid, etc., as well as additional polymers such as polyphenylene oxides, terpolymers of ethylene glycol, isophthalic acid and terephthalic acid, terpolymers of p-cyclohexanedicarboxylic acid, isophthalic acid and cyclohexylenebismethanol, copolymers of p-cyclohexanedicarboxylic acid and 2,2,4,4-tetramethylcyclobutane-1,3-diol, as well as a wide variety of additional hydrophobic polymers.

The hydrophobic, radiation-sensitive compositions described herein are advantageously coated over a portion of the image-containing hydrophilic layer. The term "portion," as used herein, refers to any portion of the hydrophilic layer. It can be either a minor portion or a major portion, the choice depending upon the desired extent of add-on image area for any given add-on image situation.

In one aspect of the present invention, a substantially hydrophobic, physically strippable layer can be interposed between the hydrophilic layer and the radiation-sensitive hydrophobic layer. The presence of such a stripping layer facilitates removal of the hydrophobic layers including an add-on image without impairing the underlying image in the hydrophilic layer. Removal is conveniently accomplished by physical separation. Solvent treatment is not required. The stripping layers are advantageously from 1 to about 25 microns in thickness, with from 1 to 10 microns being preferred. Exemplary hydrophobic substances useful in the stripping layer include such chemical species as polyethylene, cyanoethylated gelatin, film-forming polysaccharides e.g., an ether of a polysaccharide having a pyranose ring structure such as starch ether), gum arabic, sodium alginate, pectin, cellulose acetate hydrogen phthalate, hydroxyethylcellulose and poly(methacrylic acid). When coated in a very thin layer, advantageous strippable layers can also be comprised of such compounds as plasticized methyl cellulose, ethyl cellulose, methylmethacrylate or butylmethacrylate.

Alternatively, a physically strippable capability for the hydrophobic radiation-sensitive layer can be promoted without the use of an intervening strippable layer by decreasing adhesion between the hydrophilic layer and the superposed hydrophobic radiation-sensitive layer. This effect can be advantageously accomplished in at least two ways. In one aspect, an agent can be added to the hydrophobic radiation-sensitive composition which, after coating, produces discontinuities in the hydrophobic film and, in effect, decreases the total contact area between hydrophilic and hydrophobic layers and thereby lowers total adhesion. Suitable agents include substantially transparent pigment materials such as colloidal silica, colloidal titanium dioxide and the like, although a wide variety of suitable alternative materials are available. In another aspect, total adhesion can be decreased by utilizing a binder material exhibiting substantially lower adhesion, such as a silicone resin, or by introducing an adhesion decreasing material, such as a plasticizing agent, into a binder material which would otherwise possess an adhesive quality in excess of that required for advantageous physical strippability. Exemplary plasticizers include such compounds as magnesium stearate, dioctylphthalate, tricresylphosphate and the like.

As mentioned hereinabove, the photographic elements of this invention are conveniently prepared according to the subject process by coating a hydrophilic layer bearing support, such as those described elsewhere herein, with one of the above-mentioned photographic image-forming compositions. Coating is typically by solvent coating means since it offers the potential for rapid, convenient, continuous operation. Coating is effected by first dissolving the photographic image-forming composition in a suitable solvent, along with a matrix polymer if desired. Exemplary matrix polymers are described hereinabove. The coating solution for the hydrophobic layer conventionally contains from about 5 to about 20 weight percent solids, and preferably from about 8 to about 15 percent solids. In that solution, if a matrix polymer is utilized, the photographic image-forming components are typically included in an amount of from about 20 to about 50 parts by weight per 100 parts of polymeric binder, with concentrations in the range of from about 25 to about 45 parts per 100 parts of matrix polymer being preferred. Wider variations are possible where desired, but the above-mentioned ratios are typical for most conventional preparations. After coating by such means as are described above, typically at a wet thickness of from about 0.001 inch to about 0.005 inch, the coated material is dried to prepare a composite photographic element of this invention. The interpositioned stripping layer is also conveniently solvent coated by means such as those described herein for the radiation-sensitive hydrophobic layer.

In a related manner, an aqueous absorbing layer (such as a hydrophilic layer) can be coated with an aqueous solution containing a light-sensitive, image-forming diazo-type composition. The aqueous absorbing layer can be one such as hydrolyzed cellulose acetate, paper including cardboard stock and conventional photographic paper support materials. In operation, the aqueous solution containing a diazonium salt sensitizer is imbibed into a water absorbing layer such as those described immediately hereinabove and also including hydrophilic layers such as those which are advantageous in the practice of the present invention. Application of the aqueous solution is carried out merely by contacting it against an adsorbent surface. After drying, the diazo-type composition can be imagewise exposed and processed with an alkaline medium such as ammonia vapor to define an add-on photographic image. The images so prepared are transferable by dielectric heating techniques preferably where the hydrophilic material is transferred simultaneously.

To obtain an add-on photographic image on a photographic element of this invention, the coated light-sensitive material is first exposed to an imagewise pattern of activating radiation, such as visible light, ultraviolet light, etc., and thereafter treated with a developing means to prepare a visible photographic image additional to that image previously present on the visible-image-bearing material.

The developing means useful herein vary with the particular photographic image-forming composition involved. Where that composition is a diazo-type variety, treatment to develop an image conventionally involves treatment of the diazo-type composition with an alkaline medium such as, for example, exposure to aqueous ammonia vapors at ambient pressure or to high-pressure anhydrous ammonia gas, such as described in U.S. Pat. No. 3,421,895. Where the photographic image-forming composition is either a furfurylidene composition, a composition containing a protected aldehyde, or a composition containing the leuco form of a dye and an activator compound containing a carbonyl moiety, the developing means is advantageously heating the photographic image-forming composition from about 100° to about 150° C. whereupon an image is formed in the previously exposed areas. Where the photographic image-forming composition is one including the leuco form of a dye and a 2,4,5-triarylimidazolyl dimer such as those described herein, image development is accomplished directly upon exposure to activating radiation which in the case of this image-forming composition is an ultraviolet exposure. With a 2,4,5-triarylimidazolyl dimer activator, however, subsequent to the coincident exposure and image formation, the photographic image obtained is suitably stabilized or fixed either by treatment with hydroquinone to inactivate previously unreacted 2,4,5-triarylimidazolyl dimer or by washing with water to remove the unreacted leuco dye compound.

In the hydrophobic radiation-sensitive layers described herein, the hydrophobic composition including hydrophobic matrix polymers is advantageously soluble in a solvent which does not deleteriously affect the underlying image in the hydrophilic layer. The light-sensitive layer so coated is then removable, whether undeveloped or developed to an add-on photographic image, so that the light-sensitive layers or add-on images can be removed or substituted as desired. In this

fashion, any number of distinct add-on images can be prepared by removal of the previous add-on image. Removal is conveniently accomplished merely by treating the light-sensitive layer with the appropriate solvent and gently wiping the layer from the previously coated visible image-bearing material. Solvent impregnated swabs or cloths are particularly advantageous for facilitating removal of the polymeric matrix and photographic image-forming composition dispersed therein.

The criterion for advantageous add-on image removal is preservation of the underlying image in the hydrophilic layer. Accordingly, depending on the composition of that image, a variety of or at least varying solvents can be required. The only requirement is that the solvent selected is a solvent for the hydrophobic layer but not for the underlying image or for the support material.

As an example, if the image-bearing material is a photographic print or transparency, the silver or colored dye image material is usually dispersed in a hydrophilic binder such as gelatin. With such a binder present in the image-bearing material, advantageous solvents for the add-on image matrix-polymer include such organic solvents as ketones like methylethyl ketone, methylisobutyl ketone, isopropanone, cyclohexanone, etc.; alkanols like methanol, ethanol, butanol or isobutanol, as well as additional alcohols such as diacetone alcohol; ethers like ethyleneglycolmonomethyl ether, ethyleneglycolmonoethyl ether, etc.; as well as a wide variety of additional organic solvents like tetrahydrofuran, dioxane, toluene, acetonitrile and the like. Mixtures of the above-mentioned organic solvents are useful, for example, methylethyl ketone and tetrahydrofuran, methylethyl ketone and dioxane, methanol and toluene, ethanol and toluene, methylisobutyl ketone and tetrahydrofuran, cyclohexanone and ethanol, diacetone alcohol and toluene, diacetone alcohol and tetrahydrofuran, isopropanone and tetrahydrofuran, and tetrahydrofuran, isobutyl alcohol and toluene and the like. Still other solvents, such as acetone, for example, are not generally employed for removal of an add-on image which exists over a visible image carried in gelatin since the gelatin layer would be penetrated and upon removal of the add-on image, the underlying image would be either distorted or partially removed. However, solvents such as acetone, while not acceptable alone, can be utilized in conjunction with advantageous diluent solvents like tetrahydrofuran, typically in equal portions by weight, to provide a satisfactory removal solvent. Where the underlying image is not carried in a gelatin binder still additional solvents such as benzene, dimethylformamide or mixtures thereof can be used for advantageous add-on image removal without degrading the preexisting, underlying image. Additionally, the above-mentioned useful solvents can be employed in a wide variety of mixtures to provide particularly desirable removal of individual matrix polymers. Image removal can also be accomplished in many instances, by physically stripping the layer containing the add-on image from the underlying visible image-bearing material without the use of a solvent to aid in removal. This is particularly true when a stripping layer, such as those described above, is interposed between the hydrophilic layer and hydrophobic add-on image layer.

The following examples are included for a further understanding of the invention.

EXAMPLE 1

A light-sensitive photographic image-forming composition is prepared as follows:

2,5-diethoxy-4-morpholinobenzene-diazonium fluoroborate	7.25 g.
2-hydroxy-3-naphth-o-anisidide	7.33 g.
5-sulfosalicyclic acid	1.50 g.
colloidal silica	16.8 g.

are dispersed in a solution of:

polyvinylbutyral resin	67.10 g.
methylethyl ketone	320.0 g.
tetrahydrofuran	80.0 g.

The dispersion is promoted by agitation in the presence of ⅛-inch steel balls for a period of 30 minutes on a commercial vibrating shaker. The resultant light-sensitive dope is then hand coated as a layer, using a doctor-blade, at a wet thickness of 125 μ onto processed Eastman Color Print Film, Type 5380 (which processed film has a support on which are present hardened gelatin layers containing an imagewise distribution of colored dyes), thereby preparing a composite, light-sensitive photographic element. After air-drying the coated layer, the element is imagewise exposed for 90 seconds through a positive transparency to a 400 -watt high-pressure mercury arc held at a distance of 20 cm. from the exposure plane. After exposure, a positive colored dye image of the transparency is developed in the light-sensitive layer by treatment of that layer with moist ammonia vapors. In this fashion, a positive, add-on photographic image is superimposed on the original visible image-bearing material, that being the processed color print film described in this example. After formation of the add-on image, it is removed by soaking the composite element in methanol for a period of 30 seconds and then wiping gently with a soft cloth. The coating, exposure, development and removal steps are then twice repeated on the same color print film with no detrimental effect on the initial color print image. The second removal is accompanied by physically stripping the coated layer containing the add-on image from the underlying color print film. No degradation of the color print image occurs.

EXAMPLE 2

A light-sensitive, photographic element is prepared according to the procedure of example 1, except that the light-sensitive layer is coated at a wet thickness of 75 μ. Exposure is as in example 1, but for a duration of 60 seconds. Image development is as in example 1 and add-on image removal is accomplished by gently rubbing the coated layer with a paper tissue moistened with methanol.

EXAMPLE 3

A first light-sensitive coating dope is prepared as in example 1, except that the colloidal silica is deleted. A second coating dope is prepared containing:

methylmethacrylate	4 g.
methylethyl ketone	32 g.
tetrahydrofuran	8 g.

A portion of a photographic color transparency as in example 1 is coated with the second coating dope using the methods and coating thickness of example 1. After drying, this first coating is overcoated with a similar layer of the first, light-sensitive coating dope. After air-drying this layer, the resultant light-sensitive photographic element is exposed and developed as in example 1, preparing an add-on photographic image. Subsequently, the coated layers are conveniently removed by physically stripping them from the underlying hydrophilic hardened gel layers.

EXAMPLE 4

A light-sensitive, photographic image-forming composition is prepared according to the procedure of example 1 to form a dope suitable for coating, except that the chemical constituents are:

5-bromofurfurylideneazine	1.0 g.
2,4-toluenediamine	3.0 g.
iodoform	5.0 g.
polystyrene	20.0 g.
chloroform	200 ml.

Coating at a wet thickness of 125 μ is accomplished as in example 1, the support herein being a black and white photo-

graphic print (paper backing carrying a metallic silver image dispersed in hardened gelatin), and the light-sensitive layer so coated is air-dried. After drying, the composite element is exposed for 1 minute through a negative line transparency to the light of a 200-watt tungsten lamp held at a distance of 30 cm. from the exposure plane. After exposure, a visible add-on, positive photographic image is developed in the coated light-sensitive layer by heating the element to a temperature of 150° C. for a period of 90 seconds. The add-on photographic image formed thereby was subsequently removed by gentle rubbing with an adsorbent paper tissue moistened with ethanol. Multiple recoatings and removals produced no degradation of the underlying photographic silver visible image.

EXAMPLE 5

A light-sensitive, photographic image-forming composition is prepared according to the procedure of example 1 to form a dope suitable for coating, except that the chemical constituents are:

2(4-dimethylaminophenyl)-4,5,5-trimethyl-1,3-dioxane	1.0 g.
4-aminodiphenylamine	1.0 g.
iodoform	20.0 g.
polystyrene	6.0 g.
chloroform	52 ml.

Coating at a wet thickness of 125 μ is accomplished as in example 1 utilizing a support as in example 3, and the coating is air-dried. The resultant composite element is then exposed for 15 seconds to the rays of a 7.7 k.v.a. carbon arc light source through a line negative transparency, with the light source being held at a distance of 45 cm. from the exposure plane. A visible red colored positive image is formed on exposure. Image stabilization is then accomplished by heating the composite element to 150° C. for about 90 seconds.

EXAMPLE 6

A light-sensitive, photographic image-forming composition is prepared according to the procedure of example 1 to form a dope suitable for coating, except that the chemical constituents are:

tris(4-dimethylaminophenyl)methane	0.24 g.
α, α, α-tribromoacetophenone	2.0 g.
ethylcellulose	4.0 g.
toluene	20.0 ml.

Coating at a wet thickness of 75 μ is accomplished as in example 1 on a similar support, and the coating is air-dried. The resultant composite element is then imagewise exposed for 10 seconds to the ultraviolet rays of a 300-watt ultraviolet lamp held at a distance of 30 cm. from the exposure plane. After exposure, the element is heated to about 150° C. for 30 seconds to prepare a visible image. Subsequent to image development, the overcoat layer containing the add-on image is removed by gentle rubbing with an adsorbent tissue moistened with toluene. No degradation of the underlying colored dye image occurs.

EXAMPLE 7

A light-sensitive, photographic image-forming composition is prepared as follows:

tris(4-diethylamino-o-tolyl)methane trihydrochloride	1.0 g.
2,2'-bis(o-chlorophenyl)-4,4',5,5'-tetraphenylbiimidazole	1.0 g.
benzene/N,N-dimethylformamide (1:1)	200 ml.

are admixed and whirlee coated at 500 r.p.m. on an anodized aluminum support having thereon a relief image. The coating is dried and exposed through a negative line transparency and for a period of about 10 seconds to an R-2, 300-watt photoflood lamp, rich in ultraviolet rays, held at a distance of 30 cm. from the exposure plane. An intense blue positive, add-on image is produced on exposure. The element, carrying the resultant add-on image is then immersed in a saturated ether solution of hydroquinone to stabilize the image against background printout.

The invention has been described in detail with particular reference to certain preferred embodiments thereof, but it will be understood that variations and modifications can be effected within the spirit and scope of the invention.

I claim:

1. A process for preparing an add-on photographic image on a support having thereon an image in a hydrophilic colloid layer, which process comprises coating a hydrophobic, radiation-sensitive composition over a portion of the hydrophilic colloid layer, imagewise exposing the hydrophobic, radiation-sensitive composition, and thereafter developing a visible photographic image in the hydrophobic composition without substantially impairing the image in the hydrophilic colloid layer.

2. A process for preparing an add-on photographic image on a support having thereon an image in a hydrophilic colloid layer, which process comprises coating over a portion of the hydrophilic colloid layer a first, strippable layer comprising a substantially hydrophobic resin and a second layer comprising a hydrophobic, radiation-sensitive composition, imagewise exposing the hydrophobic, radiation-sensitive composition and thereafter developing a visible photographic image in the hydrophobic composition without substantially impairing the image in the hydrophilic colloid layer.

3. A process as described in claim 1 wherein the support having thereon an image in a hydrophilic colloid layer comprises a support having a photographic dye image or a photographic silver image in a hydrophilic colloid layer.

4. A process as described in claim 1 wherein the hydrophobic, radiation-sensitive composition contains a hydrophobic, film-forming resin selected from the group consisting of polymeric vinyl compounds, cellulose esters, polyphenylene oxides, homopolymers and copolymers of acrylic acid, terpolymers of ethylene glycol, isophthalic acid and terephthalic acid, terpolymers of p-cyclohexanedicarboxylic acid, isophthalic acid and cyclohexylenebismethanol and copolymers of p-cyclohexanedicarboxylic acid and 2,2,4,4-tetramethylcyclobutane-1,3-diol.

5. A process for preparing add-on photographic images on and removing add-on photographic images from a support having thereon an image in a hydrophilic colloid layer, which process comprises:

a. coating a hydrophobic, radiation-sensitive composition over a portion of the hydrophilic colloid layer,
b. imagewise exposing the hydrophobic, radiation-sensitive composition,
c. developing a visible photographic image in the hydrophobic composition, and thereafter
d. treating the exposed, image-bearing hydrophobic composition with a solvent for composition which is not a solvent for said hydrophilic colloid layer

thereby removing said exposed hydrophobic composition including the add-on photographic image contained therein, all without substantially impairing the image in the hydrophilic colloid layer.

6. A process for preparing and removing add-on photographic images on a support having thereon an image in a hydrophilic colloid layer, which process comprises:

a. coating over a portion of the hydrophilic colloid layer a first, strippable layer comprising a substantially hydrophobic resin and a second layer comprising a hydrophobic, radiation-sensitive composition,
b. imagewise exposing the hydrophobic, light-sensitive composition,
c. developing a visible photographic image in the hydrophobic composition, and thereafter

d. physically stripping the coated hydrophobic layers including the add-on photographic image from the underlying hydrophilic colloid layer to remove the add-on image without substantially impairing the image in the hydrophilic colloid layer.

7. A process for preparing an add-on photographic image on a support having thereon an image in a hydrophilic colloid layer, which process comprises:

a. coating over a portion of the hydrophilic colloid layer, a light-sensitive hydrophobic diazo-type composition containing a hydrophobic film-forming vehicle, a light-sensitive diazonium salt and a coupler compound which can react with the diazonium salt to produce an azo dye,

b. imagewise exposing the hydrophobic, light-sensitive diazo-type composition, and thereafter

c. developing a visible photographic azo dye image in the hydrophobic composition without substantially impairing the image in the hydrophilic colloid layer.

8. A process for preparing an add-on photographic image on a support having thereon an image in a hydrophilic colloid layer, which process comprises:

a. coating over a portion of the hydrophilic colloid layer a first, strippable layer comprising a substantially hydrophobic resin and a second layer comprising a light-sensitive hydrophobic diazo-type composition containing a hydrophobic film-forming vehicle, a light-sensitive diazonium salt and a coupler compound which can react with the diazonium salt to produce an azo dye,

b. imagewise exposing the hydrophobic, light-sensitive diazo-type composition, and thereafter

c. developing a visible photographic azo dye image in the hydrophobic composition without substantially impairing the image in the hydrophilic colloid layer.

9. A process as described in claim 7 wherein the support having thereon an image in a hydrophilic colloid layer comprises a support having a photographic dye image or a photographic silver image in a hydrophilic colloid layer.

10. A process as described in claim 7 wherein the light-sensitive hydrophobic diazo-type composition contains a hydrophobic, film-forming vehicle selected from the group consisting of vinyl polymers, cellulose esters, polyphenylene oxides, homopolymers and copolymers of acrylic acid, terpolymers of ethylene glycol, isophthalic acid and terephthalic acid, terpolymers of p-cyclohexanedicarboxylic acid, isophthalic acid and cyclohexylenebismethanol, and copolymers of p-cyclohexanedicarboxylic acid and 2,2,4,4-tetramethylcyclobutane-1,3-diol.

11. A process as described in claim 7 wherein the light-sensitive hydrophobic diazo-type composition contains as the image-forming components, a light-sensitive benzene diazonium salt and a phenolic coupler compound which can react with the diazonium salt to produce an azo dye.

12. A process as described in claim 10 wherein the light-sensitive hydrophobic diazo-type composition contains, as the image-forming components, the light-sensitive diazonium salt 2,5-diethoxy-4-morpholinobenzenediazonium tetrafluoroborate, and as the phenolic coupler compound, 2-hydroxy-3-naphth-o-anisidide.

13. A process for preparing an add-on photographic image on a support having thereon an image in a hydrophilic gelatin layer, which process comprises:

a. coating over a portion of the hydrophilic gelatin layer, a light-sensitive hydrophobic diazo-type composition containing a hydrophobic film-forming vehicle selected from the group consisting of vinyl polymers, cellulose esters, polyphenylene oxides, homopolymers and copolymers of acrylic acid, terpolymers of ethylene glycol, isophthalic acid and terephthalic acid, terpolymers of p-cyclohexanedicarboxylic acid, isophthalic acid and cyclohexylenebismethanol, and copolymers of p-cyclohexanedicarboxylic acid and 2,2,4,4-tetramethylcyclobutane-1,3-diol, a light-sensitive benzene diazonium salt and a phenolic coupler compound which can react with the diazonium salt to produce an azo dye,

b. imagewise exposing the hydrophobic, light-sensitive diazo-type composition, and thereafter

c. developing a visible photographic azo dye image in the hydrophobic composition without substantially impairing the image in the hydrophilic gelatin layer.

14. A process as described in claim 13 wherein the light-sensitive hydrophobic diazo-type composition contains, as the image-forming components, the light-sensitive diazonium salt 2,5-diethoxy-4-morpholinobenzenediazonium fluoroborate, and as the phenolic coupler compound, 2-hydroxy-3-naphth-o-anisidide.

15. A process for preparing an add-on photographic image on a photographic transparency having a hydrophilic-hardened gelatin layer containing a photographic dye image, which process comprises:

a. coating over a portion of the hydrophilic gelatin layer, a light-sensitive hydrophobic diazo-type composition containing a hydrophobic film-forming resin comprising poly(vinyl butyral), a light-sensitive diazonium salt comprising 2,5-diethoxy-4morpholinobenzenediazonium fluoroborate and a phenolic coupler compound comprising 2-hydrox-3-naphth-o-anisidide which can react with the diazonium salt to produce a visible azo dye image,

b. imagewise exposing the hydrophobic, light-sensitive diazo-type composition, and thereafter

c. treating the diazo-type composition with ammonia vapor to develop a visible photographic azo dye image without substantially impairing the visible image in the photographic transparency.

16. A process for preparing and removing add-on photographic images on a support having thereon an image in a hydrophilic colloid layer, which process comprises:

a. coating over a portion of the hydrophilic colloid layer, a light-sensitive hydrophobic diazo-type composition containing a hydrophobic film-forming vehicle, a light-sensitive diazonium salt and a coupler compound which can react with the diazonium salt to produce an azo dye,

b. imagewise exposing the hydrophobic, light-sensitive diazo-type composition,

c. developing a visible photographic azo dye image in the hydrophobic composition, and thereafter

d. treating the exposed image-bearing hydrophobic composition with a solvent for said composition which is not a solvent for said hydrophilic colloid layer to remove said hydrophobic composition, including the add-on azo dye image without substantially impairing the image in the hydrophilic colloid layer.

17. A process for preparing and removing add-on photographic images on a support having thereon an image in a hydrophilic colloid layer, which process comprises:

a. coating over a portion of the hydrophilic colloid layer a first, strippable layer comprising a substantially hydrophobic resin and a second layer comprising a light-sensitive hydrophobic diazo-type composition containing a hydrophobic film-forming vehicle, a light-sensitive diazonium salt and a coupler compound which can react with the diazonium salt to produce an azo dye,

b. imagewise exposing the hydrophobic, light-sensitive diazo-type composition,

c. developing a visible azo dye image in the hydrophobic composition, and thereafter

d. physically stripping the coated hydrophobic layers from the underlying hydrophilic colloid layer to remove the add-on image without substantially impairing the image in the hydrophilic colloid layer.

18. A photographic element for the production of add-on photographic images, said element comprising a support having thereon a visible image in a hydrophilic colloid layer of which a portion is overcoated with a hydrophobic light-sensitive diazo-type layer containing a hydrophobic film-forming vehicle, a light-sensitive diazonium salt and a coupler compound which can react with the diazonium salt to produce an azo dye.

19. A photographic element as described in claim 18 wherein an intervening substantially hydrophobic resin layer is present between the hydrophilic colloid layer and the hydrophobic, light-sensitive diazo-type layer.

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